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Hardness study of titanium nitride thin films deposited on bell-metal by cylindrical magnetron sputtering

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Abstract Deposition of thin films by reactive magnetron sputtering is a very suitable method for the surface protection of materials Titanium nitride thin film coatings provide very good protection to materials from wear and tear, corrosion oxidation *etc* Thin films of titanium nitride deposited by reactive magnetron sputtering in argon/nitrogen gaseous mixture acts as hard protective coating and also prevent the bell metal substrate from reacting with the environment and getting oxidized An investigation on the hardness of titanium nitride films deposited by reactive magnetron sputtering has been carried out by the method of nano indentation and an analysis of the films for different deposition conditions is presented The TiN film hardness is found to increase 13 times at 50% nitrogen in the gaseous mixture

Keywords Titanium nitride cylindrical magnetron sputtering hardness

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1. Introduction

Sputtering deposition has become a generic name for a variety of sputtering processes Among the various sputtering processes, the one, which is most widely used today, involves the use of magnetic field perpendicular to the electric field and is known as magnetron sputtering Magnetron sputtering uses confinement of excited plasma in crossed magnetic and electric fields that results in high deposition rates and good reproducibility [1,2]. Titanium nitride is a rocksalt structure (NaCl), the compound consisting of Ti atoms filled in fcc based lattice with all octahedral sites filled with nitrogen atoms Some of its physical properties are as follows Lattice parameter 0 424 nm, Melting point 3173 K, Thermal stability (ΔH^{298}) 336 6 kJmol^{-1}, Young's modulus 450 GPa TiN thin films have found applications in hard, decorative, wear and corrosion resistant coatings and also

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diffusion barriers in IC technology [3] Further, it has good electrical, thermal, mechanical and chemical properties. In micro-electronics instrumentation, it finds application for its electrical characteristics and for its diffusion barrier properties [4] Study of TiN deposition has generated a lot of interest among the scientific community because of its lustrous golden yellow coloured film which has been used for decorative applications. The golden colour of the film is due to the high reflectance of TiN at the red end of the visible spectrum with low reflectance near the ultraviolet region [5]. The formation process of TiN thin films by reactive sputtering has been studied by many researchers over the years In the case of reactively sputtered TiN film coatings, nitrogen partial pressure plays an important role in determining the mechanical properties [6]. Deposition of thin films by reactive magnetron sputtering is a very suitable method for the surface protection of materials Reactive magnetron sputtering is used for the elaborate study of titanium nitride thin films [7] Here, we have presented an analysis of the hardness study of TiN thin film deposited on bell-metal in reactive Ar/N_2 gas environment by direct current magnetron sputtering method.

2. Details

A. Experimental set up and procedure :

The experimental cylindrical magnetron device is a stainless steel chamber having dimensions of 30 cm in diameter and 100 cm in length A small titanium cylinder of length 25 cm and outer diameter 3.25 cm is placed co-axially inside the chamber which acts as the cathode For deposition of TiN, the bell metal substrates of size 0.8 cm x 0 8 cm are placed at a distance of 8 cm below the cathode A schematic diagram of the experimental set up is shown in Figure 1. For generation of a steady axial magnetic field,

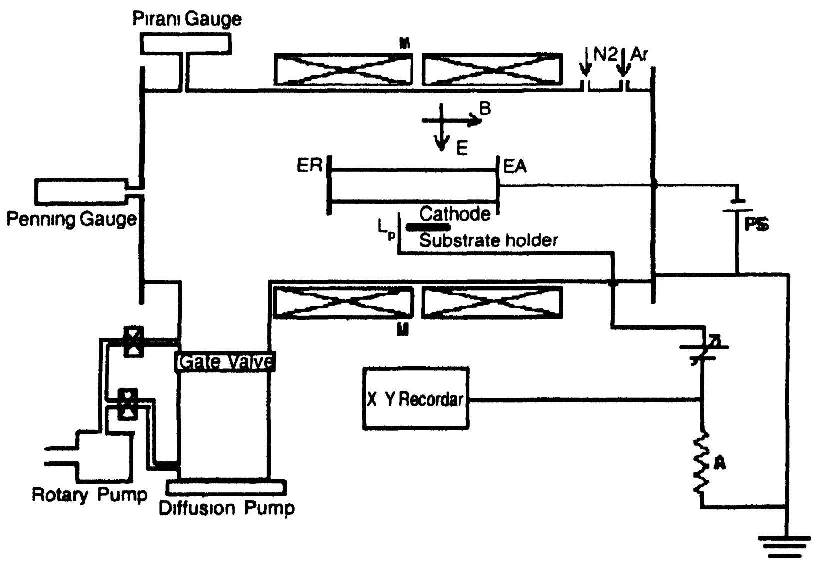

Figure 1. Schematic diagram of experimental set-up E–electric field, B–Magnetic field, ER–End reflectors, Lp–Langmuir probs, MM–Magnetic coils, PS–Power supply

two coils are placed around the body of the chamber similar to Helmholtz coils type configuration Low pressure is created inside the chamber using a combination of rotary and diffusion pumps The base pressure of the chamber is of the order of 10^{-6} Torr and working gas pressure is of the order of 10^{-3} Torr A pirani gauge and an ionization gauge are used for measurement of pressure inside the chamber The discharge power is supplied from a stabilized DC power supply (1500 V, 5 A) working in the voltage-regulated mode Gas is injected to the chamber to raise the neutral pressure up to 10^{-3} Torr by using a double valve system consisting of a stop valve and a needle valve (fine control) The deposition condition of the TiN films is as follows – discharge voltage is 600 V magnetic field is 0.01 Tesla and total gas pressure is 2×10^{-3} Torr The deposition time is 75 minutes.

B. Results and discussions :

X-ray diffraction study of the deposited titanium nitride thin films at different nitrogen percentages [(a)–25% N_2, (b) 50% N_2, (c) –75% N_2 and (d)–100% N_2] in the gas mixture shows that single phase TiN thin films have been deposited over the bell-metal substrates for each of the different deposition conditions A clear sharp and intense peak of TiN corresponding to (200) lattice texture has been observed as shown in Figure 2

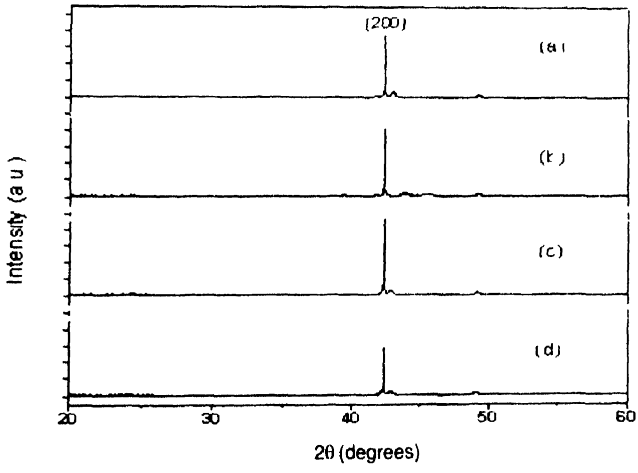

Figure 2. XRD plots of TiN at (a) - 25% N_2 (b) 50% N_2, (c) 75% N_2 and (d) 100% N_2

The surface morphology of the TiN thin films has also been studied using the atomic force microscope. Careful observation of these films shows that the film growth over the bell-metal substrate maintains a uniform pattern throughout and that they have good adherence to it The average roughness of the films is found to be of the order of 20 nm All the films exhibit dense columnar structure.

Mechanical properties of the deposited thin film coatings, like hardness and Young's modulus has been studied using the nano-indentation technique For obtaining maximum hardness, the indentor's depth of penetration was about one tenth of the deposited film's thickness. This was done so that the calculated value was a true measurement of the coating hardness. A typical indentation depth profile done by the nano-indenter on the film coating is shown in Figure. 3.

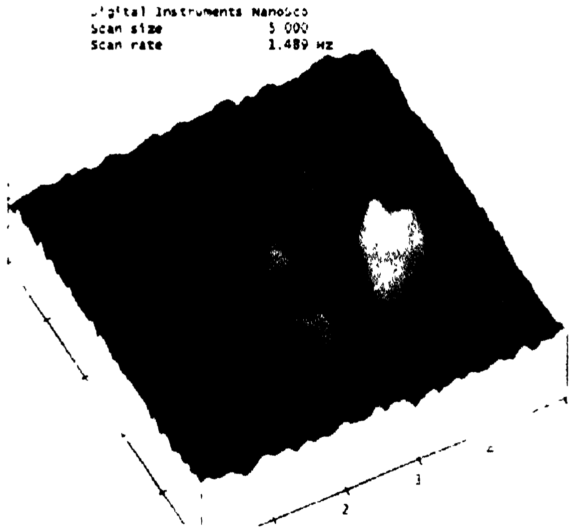

Figure 3. Image showing the indent profile on TiN sample

Figure 4 shows the applied load *versus* the corresponding indentation depth profile for the deposition of TiN thin film coating at 50% N_2 in the gas mixture. It is clearly seen that with increasing load there is a gradual deviation of the loading curve away from its initial position. This explains the property of plastic deformation wherein the material loses its elastic property. The deviation is found to be minimum at this deposition condition.

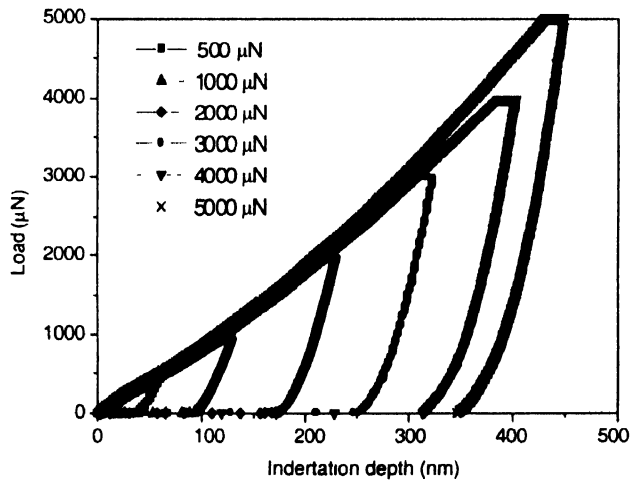

Figure 4. Load *vs* indentation depth curves at different loads.

The hardness, *H* of the deposited TiN thin films at different nitrogen percentages (25%, 50%, 75%) in the gas mixture has been calculated using the method of Oliver and Pharr

(1992), according to the relation

$$H = P_{max}/A \tag{1}$$

where P_{max} is the peak indentation load and A is the indentation contact area, determined from the indenter shape function Generally, loading data are influenced more by the material's plastic properties while the unloading data by the elastic properties Hardness is calculated from the loading data of the curves Generally the hardness values determined by nanoindentation method are functions of surface roughness chemical state of the surface layer and indenter size effect Proper care is taken to minimize the influence of these effects on the hardness value

In Figure 5, the variation of hardness and the Young's modulus with different N percentages in the gas mixture is shown It is found that the maximum hardness of the film is at 50% N_2 in the gas mixture The TiN film coating at this condition increases the hardness of bell-metal by nearly 13 times The increase in the film's hardness is an important property as it increases the durability of the material The Young's modulus value is also highest at 50% N_2 in the plasma gaseous environment

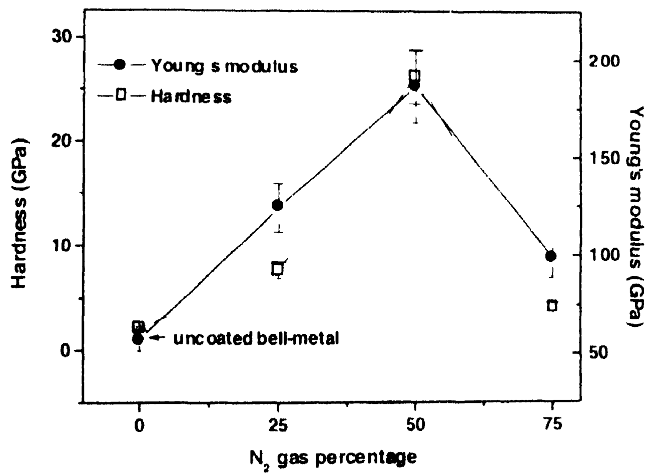

Figure 5. Plot of Hardness and Young s modulus at different N_2% in the gas mixture

3. Summary

Titanium nitride thin films have been deposited on bell-metal by reactive sputtering in cylindrical magnetron device in argon and nitrogen gas mixtures Nitrogen gas percentage in the mixture plays a significant role in the quality of the deposited film XRD analysis shows that single phase TiN films corresponding to (200) lattice texture has been formed under the above deposition condition The optimum deposition condition for the best quality titanium nitride thin film is found to be at 50% nitrogen in the gas mixture Hardness study shows that maximum hardness occurs for the film deposited at 50% nitrogen in the gas mixture. Apart from its hardness property, the radiant golden colour of these films makes it suitable to be used commercially for decorative applications

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